

# Purification and Characterisation of Organic Compounds

# PURIFICATION OF ORGANIC COMPOUNDS

Purification means removal of undesirable impurities associated with a particular organic compound, i.e., to obtain the organic compound in pure state.

The methods commonly used for the separation and purification of organic compounds are:

- (I) Crystallisation:
  - (i) Simple crystallisation
  - (ii) Fractional crystallisation
- (II) Sublimation:
- (III) Distillation:
  - (i) Simple distillation
  - (ii) Fractional distillation
  - (iii) Vacuum distillation
  - (iv) Steam distillation
- (IV) Solvent extraction
- (V) Chromatography

## Methods Employed for Purification of Solids:

The methods employed depend on the physical state of the compound.

**1. CRYSTALLISATION:** This method is based on the differences in the solubility of the organic compound and its impurities in a solvent.

- It is of two types.
- (i) Simple Crystallisation: The complete operation of simple crystallisation involves the following steps:
  - (a) **Preparation of the solution:** Organic substance is powered and is dissolved in a suitable solvent by heating. The amount of solvent should be just sufficient to dissolve the whole of the solid on heating.
  - (b) Selection of a suitable solvent: The choice of solvent is very important in the crystallisation process. The main conditions of the solvent are:
    - (i) The organic substance should dissolve in the solvent upon heating and it should get separated on cooling.
    - (ii) The solvent should not dissolve the impurities.
    - (iii) The solvent should not react chemically with the substance.

*Example:* suppose we want to purify sugar containing an impurity of common salt. This can be done by treating the mixture with ethanol around 350 K. The sugar will dissolve whereas common salt remains insoluble.

- (c) Filtration of the hot solution: The hot saturated solution is filtered preferably through a fluted filter paper placed in a glass funnel. The use of the fluted filter paper makes the filtration rapid. The jacket of the hot water funnel is heated from outside and this keeps the solution hot in the glass funnel. This will prevent the formation of crystals during filtration.
- (d) Crystallisation: The hot filtrate is allowed to cool slowly and undisturbed in a beaker or in a crystallising dish. After some time the crystals of the pure compound are formed.

- (e) Separation of the crystals: The crystals formed are separated from the mother liquor by filtration. The filtration is normally done by use of Buckner funnel and a suction pump. This enables the filtration under reduced pressure and is therefore, quite fast.
- (f) Drying of crystals: The crystals are dried by pressing between the folds of filter paper and then placed in a steam of air oven for some time. The crystals are finally dried over sulphuric acid or calcium chloride in a desiccator.

Example: (i) Sugar mixed with common salt can be purified with ethanol.

- (ii) Phthalic acid mixed with naphthalene can be purified with hot-water.
- (ii) Fractional Crystallisation: The method is used for the separation of a mixture of two compounds which are soluble in the same solvent but their solubilities are different. The hot saturated solution of the mixture is allowed to cool when the less soluble component crystallizes out earlier than separated from time to time. These fractions are now separately put to crystallisation. A series of repeated crystallisations separate the two compounds in pure form.

**2. SUBLIMATION:** Certain organic solids directly change from solid to vapour state on heating. This process is called sublimation. The vapours on cooling change back to the solid form

Solid 
$$\xrightarrow{\text{Heat}}$$
 Vapours

The sublimation process is used for the separation of those solids which sublime on heating from non-volatile solids. The process is generally used for the purification of camphor, naphthalene, anthracene, benzoic acid, etc. containing non-volatile impurities.

#### Methods Employed for purification of Liquids:

**3. DISTILLATIOIN:** Distillation is a process which involves two steps:

- (i) Vaporisation: Liquid is converted into vapours.
- (ii) Condensation: Vapours are condensed again into liquid.
- (a) **Simple distillation:** This method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. The simple distillation involves its boiling point so that it is converted into vapours. On cooling the vapours, pure liquid is obtained.

The distillate contains pure liquid while the impurities are left behind in the distillation flask.

- Examples (1) Ether and ethyl alcohol
  - (2) Benzene and aniline
  - (3) Chloroform and aniline
  - (4) Ether and toluene
- (b) Fractional Distillation: This process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. The fractionating column is a long tube provided with obstructions to the passage of the vapours moving upwards and liquid moving downwards.

Since in this process, the distillate is collected in fractions under different tempratares, it is known as Fractional distillation.

This method may be used to separate a mixture of

- (1) Acetone (b.p. 330K) and methyl alcohol (b.p. 338K)
- (2) Benzene and toluene
- (c) Distillation Under Reduced Pressure (Vacuum Distillation): Certain liquids tend to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation. Therefore, vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.
  - Cane juice can also be concentrated by this method.
  - This technique can be used to separate glycerol from spent lye in soap industry.
- (d) Steam Distillation: The process of steam distillation is used for the separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture. Thus, the process of steam distillations is used to purify the substances which

- (i) are volatile in steam but are not miscible with water;
- (ii) possess sufficiently higher vapour pressure at the boiling point temperature of water (100°C);
- (iii) contain non-volatile impurities.
  - Examples
    - (i) The process of steam distillation can be applied for the separation of a mixture of o-nitrophenol and p-nitrophenol.
  - (ii) The method can also be used for the purification of impure sample of aniline, Chlorotoluenes, Nitrobenzene.
  - (iii) It is also employed in the isolation of essential oils from flowers.

(4) **SOLVENT EXTRACTION:** The process of separation of an organic compound from its aqueous solution by shaking with a suitable organic solvent is termed solvent extraction. The solvent should be immiscible with water and the organic compound, to be separated should be highly soluble in it.

(5) CHROMATOGRAPHY: This method is based on the differences in the rates at which the compounds of a mixture are adsorbed on a suitable adsorbent. There are many forms of chromatography such as column chromatography, paper chromatography, thin layer chromatography (TLC), gas chromatography, etc. The simplest method is column chromatography.

# QUALTATIVE ANALYSIS

## Detection of Carbon and Hydrogen

When the mixture is heated with copper oxide the carbon present in the compound is oxidised to carbon dioxide which turns lime water milky. The hydrogen present in the organic compound is oxidised to water which turns anhydrous copper sulphate in the bulb to blue.

## Liebig's test

 $\begin{array}{l} C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu \\ 2H + CuO \xrightarrow{\Delta} Cu + H_2O \\ CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O \\ CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O \\ (white) \qquad (Blue) \\ \end{array}$ This method is known as **copper oxide test**.

# Detection of Nitrogen, Sulphur, Halogens

## Lassaigne's test

These elements are tested in an organic compound by Lassaigne's test. The organic compound (containing N, S, and/or halogens) is fused with sodium metal as to convert these elements into ionisable inorganic substances, i.e., nitrogen into sodium cyanide, sulphur into sodium sulphide and halogens into sodium halides.

Test for Nitrogen: The nitrogen in the compound reacts with sodium metal to form sodium cyanide.

$$\begin{split} &\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN} \\ &\text{FeSO}_4 + 2\text{NaCN} \longrightarrow \text{Fe}(\text{CN})_2 + \text{Na}_2\text{SO}_4 \\ &\text{Fe}(\text{CN})_2 + 4\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_6] \text{ sodium ferrocyanide} \\ &3\text{Na}_4[\text{Fe}(\text{CN})_6] + 4\text{FeCl}_3 \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{NaCl Ferric ferrocyanide (Prussian blue colour)} \end{split}$$

#### Special test for Nitrogen:

• Sodalime test: A pinch of an organic compound is heated strongly with soda lime (NaOH + CaO) in a test tube. If ammonia gas evolves, it indicated nitrogen.

$$CH_3 CONH_2 + NaOH \xrightarrow{CaO} CH_3 COONa + NH_3$$
  
acetamide

• Limitation: This method has a limitation. A large number of organic compounds such as nitro and diazo compounds do not liberate ammonia on heating with sodalime.

#### Test for Sulphur:

The sulphur in the compound reacts with sodium metal to form sodium sulphide.

$$2Na + S \longrightarrow Na_2S$$

The Lassaigne's extract is divided into two parts and following test are performed.

(a) Sodium nitroprusside test: The one portion of the extract, a few drops of sodium nitroprosside are added. The appearance of violet colouration indicates sulphur.

$$\begin{array}{c} Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NO\cdot S] \\ \text{Sodium nitroprusside} & \text{violet colouration} \end{array}$$

(b) Lead acetate test: The other part of the Lassaigne's extract is acidified with acetic acid and then lead acetate solution is added. Formation of black precipitate confirms the presence of sulphur.

$Na_2S + Pb(CH_3COO)_2$ —	$\rightarrow PbS + 2CH_3COONa$
lead acetate	onten

#### Test for Nitrogen and Sulphur Present Together:

 $Na + C + N + S \longrightarrow NaCNS$  $Fe^{3+} + 3CNS^{-} \longrightarrow Fe(CNS)_{3}$ Blood red colour

#### Test for Halogens:

Sodium will combine with the halogen (from the organic compound) to form sodium halide

 $Na + X \xrightarrow{Fusion} NaX(X = Cl, Br, I)$ 

(i) A white precipitate soluble in ammonium hydroxide solution indicates the presence of chlorine in the organic compound

 $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$ white ppt.

(ii) A dull yellow precipitate partially soluble in ammonium hydroxide solution indicates the presence of bromine in the organic compound.

 $NaBr + AgNO_3 \longrightarrow AgCl + NaNO_3$ dull yellow ppt.

(iii) A bright yellow precipitate, completely insoluble in ammonium hydroxide solution, indicates the presence of iodine in the organic compound.

 $NaI + AgNO_3 \longrightarrow AgI + NaNO_3$ bright yellow ppt.

#### Special test for bromine and iodine (Layer test):

 $2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$ (turns CS<sub>2</sub> layer orange)

 $\begin{array}{ccc} 2NaI + Cl_2 & \longrightarrow & 2NaCl + I_2 \\ & (turns \ CS_2 \ layer \ violet) \end{array}$ 

#### Test for phosphorus:

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compounds is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

 $Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$ 

# QUANTITATIVE ANALYSIS

1. Estimation of Carbon and Hydrogen: By Liebig combustion method.



## 2. Estimation of Nitrogen:

There are two methods for the estimation of nitrogen.

(i) Duma's method

$$\therefore \% \text{ of } N = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at } N.T.P}{\text{Mass of organic compound}} \times 100$$

- (ii) Kjeldahl's method: This method cannot be used for
  - (i) organic compounds containing nitrogen in the ring such as pyridine, quinoline, etc.
  - (ii) Organic compounds containing nitrogen  $(-NO_2)$  and diazo (-N = N-) groups.

% of N = 
$$\frac{1.4 \times N \times V}{W}$$

- N = Normality of acid.
- V = volume of acid used for neutralization of  $NH_3$ .
- W = Weight of organic substance.
- 3. Estimation of Halogens: By Carius method.

% of X = 
$$\frac{\text{Atomic mass of halogen} \times \text{Mass of silver halide}}{(108 + \text{At. mass of halogen}) \times \text{Mass of organic substance}} \times 100$$

(i) % of Cl = 
$$\frac{35.5}{143.5} \times \frac{\text{Mass of AgCl}}{\text{Mass of organic substance}} \times 100$$

(ii) % of Br = 
$$\frac{80}{188} \times \frac{\text{Mass of AgBr}}{\text{Mass of organic substance}} \times 100$$

(iii) % of I = 
$$\frac{127}{235} \times \frac{\text{Mass of AgI}}{\text{Mass of organic substance}} \times 100$$

4. Estimation of Sulphur: By Carius method.

% of <b>S</b> –	32	Mass of BaSO <sub>4</sub>	$\sim 100$
// 01 5 -	233 ^	Mass of organic compound	~ 100

5. Estimation of Phosphorus: By Carius method.

% of D -	62	Mass of Magnesium pyrophosphate	20
$\frac{10011}{2}$	222 ^	Mass of organic compound	0

## SOLVED EXAMPLE

- 1. In sodium fusion test of organic compounds, the nitrogen of an organic compound is converted to
  - (1) Sodamide (2) Sodium cyanide
  - (3) Sodium nitrite (4) Sodium nitrate
- Sol. [2]

 $Na + C + N \xrightarrow{fusion} NaCN$ 

- 2. The quantitative determination of halogen in an organic compound is known as:
  - (1) Duma's method (2) Carius method
  - (3) Kjeldahl's method (4) Liebig method
- Sol. [2]

The quantitative determination of halogen in an organic compound is called as Carius method.

3. In a Dumas experiment, 0.5 g of an organic compound on heating with copper oxide liberated 112 mL of N<sub>2</sub> at STP. The percentage of nitrogen (by weight) in the compound is:

(1)	70		(2)	35

Sol. [4]

% N = 
$$\frac{28}{24000}$$
  $\frac{\text{vol. of N}_2(\text{ml})}{\text{wt. of organic subs.}} \times 100$   
=  $\frac{28}{22400} \times \frac{122}{0.5} \times 100 = 28\%$ 

4. An organic compound gave C = 92.31% and H = 7.69% If molecular weight of the compound is 78, its molecular formula is

(1)	$C_6H_6$	(2)	$C_7H_7$
(3)	$C_{6}H_{18}$	(4)	C <sub>8</sub> H <sub>20</sub>

(3) 
$$C_6 H_{18}$$
 (4)  $C_8$ 

Sol. [1]

Element	Percentage	Atomic Mass	Relative number of atoms	Simplest ratio of atoms
Carbon	92.31	12	$\frac{92.31}{12} = 7.69$	$\frac{7.69}{7.69} = 1$
Hydrogen	7.69	1	$\frac{7.69}{1} = 7.69$	$\frac{7.69}{7.69} = 1$

Empirical formula = CH

Molecular formula =  $(CH)_n$ 

$$(12 + 1) \times n = 78$$

$$n = \frac{78}{13} = 6$$

Thus, the molecular formula =  $C_6H_6$ 

- 5. Aniline has high boiling point, high vapour pressure at 100°C and is insoluble in water. Aniline is therefore, separated by:
  - (1) Steam distillation
  - (2) Simple distillation
  - (3) Distillation at low pressure
  - (4) Sublimation
- Sol. [1]

Aniline separated by steam distillation.

- 6. The most suitable method for separation of 1:1 mixture of ortho- and para nitrophenols is:
  - (1) Distillation (2) Crystallisation
  - (3) Sublimation (4) Chromatography
- Sol. [1]

Due to intramolecular H-bond in o- nitrophenol its volatile nature increases so that separated by distillation.

7. 0.099 g of an organic compound when heated with fuming nitric in the presence of silver nitrate in a Carius tube gave 0.287 g silver chloride. The percentage of chlorine in the compound is about:

Sol. [2]

$$\% = \text{Cl} = \frac{35.5}{143.5} \times \frac{\text{wt. of AgCl}}{\text{wt. of organic compound}} \times 100$$

$$= \frac{35.5}{143.5} \times \frac{.287}{.099} \times 100$$

= 71.72%

8. In Lassaigne's test the organic compound is fused with sodium metal to:

- (1) Ignite the compound
- (2) Oxidise the compound
- (3) Convert the elements in ionic form
- (4) Reduce the compound

Sol. [3]

 $Na + C + N \longrightarrow NaCN$ 

(covalent) (Ionic)

- **9.** The Lassaigne's extract is boiled with conc.  $HNO_3$  while testing for the halogens. By doing so it:
  - (1) decomposes Na<sub>2</sub>S and NaCN, if formed
  - (2) helps in the precipitation of AgCl
  - (3) increases the solubility product of AgCl
  - (4) increases the concentration of  $NO_3$  ions

#### Sol. [1]

Before the test of halogen, Lassaigne's extract is boiled with conc.  $HNO_3$  to remove  $Na_2S$  and NaCN in form of  $H_2S$  and HCN.

- **1.** A compound which does not give a positive test in the Lassaigne's test for 'N' is
  - (1) Glycine
     (2) Phenyl hydrazine
     (3) Urea
     (4) Azobenzene
- **2.** 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582 g of BaSO<sub>4</sub>. The percentage of sulphur in the compound is

(1) 20.24	(2)	35
-----------	-----	----

- (3) 40 (4) 45
- 3. Liebig method is used for the estimation of
  - (1) Nitrogen (2) Sulphur
  - (3) Carbon and hydrogen (4) Halogens
- **4.** The latest technique for the purification of organic compounds is
  - (1) Fractional distillation (2) Chromatography
  - (3) Vacuum distillation (4) Crystallization
- 5. p-nitrophenol and o-nitrophenol are separated by
  - (1) Crystallisation
  - (2) Fractional crystallisation
  - (3) Distillation
  - (4) Steam distillation
- **6.** In the estimation of sulphur organic compound on treating with conc. HNO<sub>3</sub> is converted to
  - (1)  $SO_2$  (2)  $H_2S$
  - (3)  $H_2SO_4$  (4)  $SO_3$
- 7. How will you separate a solution (miscible) of benzene + CHCl<sub>3</sub>?
  - (1) Sublimation (2) Filtration
  - (3) Distillation (4) Crystallisation

- 10. In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of compound neutralised 10 mL of 1 M  $H_2SO_4$ . The percentage of nitrogen in the soil is:
  - (1) 37.33 (2) 45.33
  - (3) 35.33 (4) 43.33
- Sol. [1]

% N =  $\frac{1.4 \text{ NV}}{W}$ 10 mL 1M H<sub>2</sub>SO<sub>4</sub> ≡ evolved NH<sub>3</sub> ∴ V = 10 mL N = n factor × M = 2 × 1 = 2N %N =  $\frac{1.4 × 2 × 10}{0.75}$  = 37.33%

- EXERCISE 1
  - **8.** In Lassaigne's test for the detection of nitrogen in an organic compound, the appearance of the Prussian blue colour is due to the formation of:
    - (1)  $NaFe^{III}[Fe^{II}(CN)_6]$  (2)  $NaFe^{II}[Fe^{III}(CN)_6]$
    - (3)  $Fe_4[Fe(CN)_6]_3$  (4)  $Na_4[Fe(CN)_6]$
  - **9.** Fractional crystallisation is carried out to separate such mixtures:
    - (1) Organic solids mixed with inorganic solids
    - (2) Organic solids highly soluble in water
    - (3) Organic solids having small difference in their solubility in suitable solvent
    - (4) Organic solids having great difference in their solubility in suitable solvent
  - **10.** AgNO<sub>3</sub> solution does not give white ppt. with CCl<sub>4</sub> but with sodium extract of CCl<sub>4</sub>, AgNO<sub>3</sub> gives white precipitate because:
    - (1)  $CCl_4$  is covalent compound
    - (2)  $CCl_4$  is partially ionised
    - (3) Sodium extract of  $CCl_4$  contains  $Cl^-$  ions and  $Na^+$  ion
    - (4) Sodium extract of  $CCl_4$  contains  $ClO_3^-$  ions
  - **11.** If the sodium extract of an organic compound develops a blood red colour on treatment with FeCl<sub>3</sub> solution, which of the following ions must be present in the sodium extract that responds to this colour test?
    - (1)  $CN^{-}$  (2)  $CNO^{-}$
    - (3)  $CNS^{-}$  (4)  $S^{2-}$
  - 12. In Kjeldahl's method of estimation of nitrogen,  $K_2SO_4$  acts as:

- (1) an oxidising agent (2) catalytic agent
- (3) hydrolysing agent (4) boiling point elevator
- 13. To detect iodine in presence of bromine, the sodium extract is treated with  $NaNO_2$  + glacial acetic acid +  $CCl_4$ . Iodine is detected by the appearance of
  - (1) yellow colour of  $CCl_4$  layer
  - (2) purple colour of  $CCl_4$
  - (3) brown colour in the organic layer of  $CCl_4$
  - (4) deep blue colour in  $CCl_4$

**14.** Lassaigne's test for the detection of nitrogen will fail in the case of

	(1) $NH_2CONH_2$	(2) $NH_2CONHNH_2.HCl$
	(3) NH <sub>2</sub> NH <sub>2</sub> .HCl	(4) $C_6H_5NHNH_2.2HCl$
15.	In Kjeldahl's method,	nitrogen present is estimated
	as	
	(1) N <sub>2</sub>	(2) NH <sub>3</sub>
	(3) NO <sub>2</sub>	(4) None of these

#### **EXERCISE 2**

- **1.** In Lassaigne's test for nitrogen, the blue colour is due to the formation of
  - (1) Ferric ferrocyanide
  - (2) Potassium ferrocyanide
  - (3) Sodium ferrocyanide
  - (4) Sodium cyanide
- **2.** 73 g of an amide obtained from a carboxylic acid, RCOOH, liberated 17 g of ammonia upon heating with alkali. The acid is
  - (1) Formic acid (2) Acetic acid
  - (3) propionic acid (4) benzoic acid
- **3.** Anhydrous formic acid cannot be obtained from its aqueous solution by simple fractional distillation because
  - (1) Pure HCOOH is unstable
  - (2) HCOOH forms hydrogen bonds with water
  - (3) Boiling point of HCOOH is very close to that of water
  - (4) Constant boiling azeotropic mixture is formed with water
- **4.** In Kjeldahl method function of CuSO<sub>4</sub> is
  - (1) B.P. elevator
  - (2) Catalyst
  - (3) Freezing point depressor
  - (4) None of these
- **5.** If an organic compound contains both nitrogen and sulphur, its fusion with sodium converts these elements into:
  - (1) Na<sub>2</sub>S and NaCN (2) NaSCN
  - (3) Na<sub>2</sub>SO<sub>3</sub> and NaCN (4) Na<sub>2</sub>S and NaCNO

- 6. Which of the following statement s is correct ?
  - (1) Two solid organic substances are said to be different if their mixed melting point is depressed below the melting points of both of these
  - (2) Ethanol and water cannot be separated from each other completely by simple distillation as they form azeotrpic mixture.
  - (3) Impure glycerine can be purified by vaccume distillation
  - (4) All of these
- 7. Silica gel is used for keeping away the moisture because it
  - (1) Absorbs  $H_2O$  (2) Adsorbs  $H_2O$
  - (3) Reacts with  $H_2O$  (4) None of these
- **8.** Which of the following will not give test for nitrogen in Lassaigne's test?
  - (1)  $C_6H_5NHNH_2$
  - (2)  $H_2NCONH_2$
  - (3) NH<sub>2</sub>-NH<sub>2</sub>

(4) 
$$HO_3S - NH_2$$

- 9. Turpentine oil can be purified by
  - (1) Vacuum distillation (2) Fractional distillation
  - (3) Steam distillation (4) Simple distillation
- **10.** Which of the following compound will give blood red colour while doing the Lassaigne's test for N?
  - (1)  $(NH_2)_2C=O$  (2)  $H_2N(C_6H_4)SO_3H$
  - $(3) C_6H_5SO_3H \qquad (4) CHCl_3$
- EXERCISE 3

#### **Numerical Section**

1. 0.50 g of an organic compound was Kjeldahlised and the NH<sub>3</sub> evolved was absorbed in a certain volume of 1N H<sub>2</sub>SO<sub>4</sub>. The residual acid required 60 cm<sup>3</sup> of N/2 NaOH. Find the volume of 1N H<sub>2</sub>SO<sub>4</sub> taken if the percentage 6.

(1) 25	(2) 50
(3) 75	(4) 100

**2.** 0.25 g of an organic compound gave 31.1 mL, of  $N_2$  by Duma's method. Calculate the % of N in this compound.

(1)	10.20%	(2)	12.44%
(3)	15.55%	(4)	20.66%

**3.** An organic compound has carbon and hydrogen percentages in the ratio 6 : 1 and carbon and oxygen percentage in the ratio 3 : 4. The compound has the empirical formula

(1)	CH <sub>2</sub> O	(2)	$CH_4O$
(3)	$C_2H_6O$	(4)	$CHO_2$

- **4.** 0.2 g of an organic compound containing C, H and O, on combustion gave 0.147g CO<sub>2</sub> and 0.12 g water. The percentage of oxygen in organic compound is
  - (1) 73.29% (2) 78.45%
  - (3) 83.23% (4) 89.50%
- **5.** 2.79 g of an organic compound when heated in Carius tube with conc.  $HNO_3$  and  $H_3PO_4$  formed converted into MgNH<sub>4</sub>.PO<sub>4</sub> ppt. The ppt. on heating gave 1.332 g of Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. The percentage of P in the compound is
  - (1) 23.33 (2) 13.33
  - (3) 33.33 (4) 26.66
- 6. In Duma's method of estimation of nitrogen 0.35 g of an organic compound gave 55 mL of nitrogen collected at 300 K temperature and 715 mm pressure. The percentage composition of nitrogen in the compound would be (Aqueous tension at 300 K = 15 mm)

(1) 14.45 $(2)$ 15.4	(1)	14.45	(2)	15.45
----------------------	-----	-------	-----	-------

- (3) 16.45 (4) 17.45
- **7.** 0.2475 g of an organic compound gave on combustion 0.4950 g of carbon dioxide and 0.2025 g of water. The percentage of carbon and hydrogen are
  - (1) 54.54, 9.09 (2) 52.54, 8.09
  - (3) 120, 5.8 (4) None of these

## Assertion and Reason Type Question

(1) If both (A) and (R) are correct and (R) is the correct explanation for (A)

- (2) If both (A) and (R) are correct and (R) is not the correct explanation
- (3) If (A) is correct and (R) is incorrect
- (4) If (A) is incorrect and (R) is correct
- **8.** Assertion: A mixture of plant pigments can be separated by chromatography.

**Reason:** Chromatography is used for the separation of coloured substance into individual components.

**9.** Assertion: Duma's method is more applicable to nitrogen containing organic compounds than Kjeldahl's method.

**Reason:** Kjeldahl's method does not give satisfactory results for compounds in which N is linked to nitrogen.

## **Column Matching Type Question**

## 10. Column-I

(A) Kjeldahl's method (p) Empirical formula of Acetone as well as glucose.

Column-II

- (B) Nitrogen of organic (q) Nitrogen of organic compound compound is converted is into free N<sub>2</sub> gas (q) nium sulphate
- (C) Na<sub>4</sub>[Fe(CN)<sub>5</sub>NOS] (r) Compound formed in Lassaigne's test for N it sulphur is also present.
   (D) Fe(CNS)<sub>3</sub> (s) Purple colouration to
  - the Lassaigne's test for S.
- (E) Methanal (t) Duma's method.
- (1)  $A \rightarrow q$ ;  $B \rightarrow t$ ;  $C \rightarrow s$ ;  $D \rightarrow r$ ;  $E \rightarrow p$
- (2)  $A \rightarrow t$ ;  $B \rightarrow q$ ;  $C \rightarrow s$ ;  $D \rightarrow r$ ;  $E \rightarrow p$
- (3)  $A \rightarrow q$ ;  $B \rightarrow t$ ;  $C \rightarrow r$ ;  $D \rightarrow p$ ;  $E \rightarrow s$
- (4)  $A \rightarrow s; B \rightarrow r; C \rightarrow q; D \rightarrow t; E \rightarrow p$

#### **EXERCISE** 4

 The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is [JEE Mains-2004]

(1)	$Fe_4[Fe_4(CN)_6]_3$	(2) $Na_3[Fe(CN)_6]$
(2)	$\mathbf{E}_{\mathbf{r}}(\mathbf{CN})$	(4) $\mathbf{N}_{\mathbf{n}} = \mathbf{E}_{\mathbf{n}}(\mathbf{C}\mathbf{N}) \mathbf{N}_{\mathbf{O}}\mathbf{C}\mathbf{I}$

- (3)  $\operatorname{Fe}(\operatorname{CN})_3$  (4)  $\operatorname{Na}_4[\operatorname{Fe}(\operatorname{CN})_5\operatorname{NOS}]$
- **2.** The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium

hydroxide solution for complete neutralisation. The organic compound is [JEE Mains-2004]

(1) acetamide (2) benzamide

(3) urea

- (4) thiourea
- **3.** 29.5 mg of an organic compound containing nitrogen was digested accordingto Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of

0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is

59.0

#### [JEE Mains-2010]

(3) 47.4 (	(4)	23.1
------------	-----	------

- 4. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is: (atomic mass Ag = 108; Br = 80) [JEE Mains-2015]
  (1) 24 (2) 36
  (2) 40 (4) (5)
  - (3) 48 (4) 60
- 5. The hottest region of Bunsen flame shown in the figure given below is [JEE Mains-2016]



- (1) region 2 (2) region 3
- (3) region 4 (4) region 1
- **6.** The distillation technique most suited for separating glycerol from spent lye in the soap industry is

#### [JEE Mains-2016]

- (1) fractional distillation
- (2) steam distillation
- (3) distillation under reduced pressure
- (4) simple distillation

## ANSWER KEY

EXERCISE	# 1					
1. (4)	2.	(1)	3.	(3)	4. (2)	5. (4)
6. (3)	7.	(3)	8.	(3)	9. (3)	10. (3)
11. (3)	12.	(4)	13.	(2)	14. (3)	15. (2)
EXERCISE	# 2					
1. (1)	2.	(2)	3.	(3)	4. (2)	5. (2)
6. (4)	7.	(2)	8.	(3)	9. (3)	10. (2)
EXERCISE	# 3					
1. (2)	2.	(3)	3.	(1)	4. (1)	5. (2)
6. (3)	7.	(1)	8.	(2)	9. (2)	10. (1)
EXERCISE	# 4					
1. (1) 6. (3)	2.	(3)	3.	(4)	4. (1)	5. (1)

## HINT AND SOLUTION

#### EXERCISE # 1

1. [4]



Does not give positive test in Lassaigne's test for N.

2. [1] %S =  $\frac{32}{233} \times \frac{\text{wt of BaSO}_4}{\text{wt of org. Sub.}} \times 100$  $\frac{32}{233} \times \frac{.582}{.395} \times 100 = 20.24\%$ 

## 3. [3]

Liebig's method is used for the estimation of carbon and hydrogen.

## 4. [2]

The latest technique for the purification of organic compounds is chromatography

5. [4]

p-nitrophenol and o-nitrophenol are separated by steam distillation (refer Key concept)

6. [3]

 $S + HNO_3$  (fuming)  $\xrightarrow{Heat}$   $H_2SO_4$ 

7. [3]

Separation a solution (miscible) of benzene +  $CHCl_3$  by distillation

#### 8. [3]

ш

 $Na + C + N \longrightarrow NaCN$ 

 $\begin{array}{ll} \mbox{FeSO}_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4 \\ \mbox{6NaCN} + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6] + 2NaOH \\ \mbox{3Na}_4[Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl \\ \mbox{Sodium ferrocyanide} \\ \mbox{Sodium ferrocyanide} \\ \mbox{(ferric ferrocyanide)} \\ \mbox{green} \end{array}$ 

#### 9. [3]

Fractional crystallisation is carried out to separate mixtures of organic solids having small difference in their solubilities in suitable solvent. (refer Key concept)

#### 10. [3]

Sodium extract of  $CCl_4$  contains  $Cl^-$  ions and  $Na^+$  ion.

#### 11. [3]

 $Na + C + N + S \longrightarrow NaCNS$ 

$$3CNS^{\ominus} + Fe^{3+} \longrightarrow [Fe (CNS)]_3$$
  
Blood red color

## 12. [4]

On adding K<sub>2</sub>SO<sub>4</sub> boiling point increased so it is boiling point clevator.

13. [2]

# 14. [3]

NH<sub>2</sub>-NH<sub>2</sub> (Inorganic compound give -ve Lassaigne's test).

## 15. [2]

Organic compound +  $H_2SO_4(conc.) \longrightarrow (NH_4)_2SO_4$  $(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 +$  $2H_2O$ 

NH<sub>3</sub> is estimated volumetrically by titrating against standard solution of acid.

## EXERCISE # 2

1. [1]

In Lassaigne's test substance is heated strongly with sodium metal then water extract is boiled with alkaline FeSO<sub>4</sub> solution and after cooling FeCl<sub>3</sub> solution and excess of HCl is added in it. If Prussian blue or green ppt. is obtained, then nitrogen is confirmed:

 $Na + C + N \longrightarrow NaCN$ 

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

 $\begin{array}{l} 6\mathrm{NaCN} + \mathrm{Fe(OH)}_2 \longrightarrow \mathrm{Na_4[Fe(CN)_6]} + 2\mathrm{NaOH} \\ 3\mathrm{Na_4[Fe(CN)_6]} + 4\mathrm{FeCl_3} \longrightarrow \mathrm{Fe_4[Fe(CN)_6]_3} + 12\mathrm{NaCl} \end{array}$ 

ferric ferrocyanide Prussian blue

Sodium ferrocyanide (ferric ferrocyanide)

2. [2]

$$\begin{array}{c} \text{R-C-OH} \longrightarrow \text{R-C-NH}_2 \xrightarrow{\text{NaOH}} \text{NH}_3 \\ \parallel \\ \text{O} & \text{O} \end{array}$$

Equivalent of Acid  $\equiv$  Equivalent of amide = Equivalent of NH<sub>3</sub>

$$\frac{73}{\text{mol.wt.}} = \frac{17}{17}$$
  
Mol. wt. of amide = 73  
 $C_n H_{2n+1}NO$   
 $12n + 2n + 1 + 14 + 16 = 73$   
 $n = \frac{42}{14} = 3$ 

acid also must have 3C, i.e., propionic acid

## 4. [2]

CuSO<sub>4</sub> acts catalyst.

5. [2]

$$Na + C + S + N \longrightarrow NaSCN$$

6. [4]

Theory base

7. [2]

Silica gel is used for keeping away the moisture because it Adsorbs H<sub>2</sub>O.

## 8. [3]

Inorganic Substance (NH<sub>2</sub>–NH<sub>2</sub>) fails for the estimation of N by Lassaigne's List.

## 9. [3]

Turpentine oil can be purified by Steam distillation

## 10. [2]

Compound containing both N and S, will give blood red colour.

 $Na + C + N + S \longrightarrow NaCNS$  $Fe^{3+} + 3CNS^{-} \longrightarrow Fe(CNS)_3$ 

Blood red colour

# EXERCISE # 3

1. [2]

Let the vol. of 1N  $H_2SO_4$  taken = V mL. Now 60 mL of N/2 NaOH = 30 mL of 1N NaOH = 30 mL of 1N  $H_2SO_4$ Thus, vol. of acid unused = 30 mL of 1N  $H_2SO_4$  $\therefore$  Vol. of 1N H<sub>2</sub>SO<sub>4</sub> used = (V - 30) mL Now % of N is given by the relation, % of  $N = \frac{1.4 \times N_1 \times V}{W}$ or  $56 = \frac{1.4 \times 1 \times (V - 30)}{0.50}$  or V = 50 mL. 2. [3] % N (By Duma's method)  $=\frac{28 \times \text{Volume of N}_2 \text{ at NTP} \times 100}{22400 \times \text{weight of compound}}$  $-28 \times 31.1 \times 100 - 155\%$ 

3. [1]  

$$\therefore C : H : O = 6 : 1 : 8, \% C : H : O$$

$$= \frac{6}{15} \times 100 : \frac{1}{15} \times 100 : \frac{8}{15} \times 100$$

$$= 40 : 6.67 : 53.3$$

3. [3]

$$= \frac{40}{12} : \frac{6.67}{1} : \frac{53.3}{16}$$
  
= 3.33 : 6.67 : 3.33  
= 1 : 2 : 1 i.e. CH<sub>2</sub>O

$$\% C = \frac{12}{44} \times \frac{\text{wt of CO}_2}{\text{wt of org. sub}} \times 100$$
$$= \frac{12}{44} \times \frac{147}{0.2} \times 100 = 20\%$$
$$\% H = \frac{2}{18} \times \frac{\text{wt of H}_2O}{\text{wt of org. sub}} \times 100$$
$$= \frac{2}{18} \times \frac{.12}{.2} \times 100 = 6.66\%$$

$$\% \text{ oxygen} = 100 - (20 + 6.66)$$
  
= 73.3%

## 5. [2]

$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{wt. of magnesium pyrophosphate}}{\text{wt. of organic compound}} \times 100$$
$$= \frac{62}{222} \times \frac{1.332}{2.79} \times 100$$
$$= 13.33\%$$

6. [3]

Gas equation

$$\frac{\mathbf{r}_{1} \mathbf{v}_{1}}{\mathbf{T}_{1}} = \frac{\mathbf{r}_{2} \mathbf{v}_{2}}{\mathbf{T}_{2}}$$

$$\frac{700 \times 55}{300} = \frac{760 \times \mathbf{V}_{2}}{273}$$

Aqueous tension at 300 K = 15 mm

$$V_{2} = \frac{700 \times 273 \times 55}{760 \times 300}$$
  
= 46 mL at N.T.P.  
∴ % of N =  $\frac{28}{22400} \times \frac{\text{Volume of N}_{2} \text{ at N.P.T}}{\text{Mass of organic compound}} \times 100$   
% N =  $\frac{28}{22400} \times \frac{46}{.35} \times 100 = 16.45\%$ 

## 7. [1]

Wt. of organic compound = 0.2475 g Wt. of CO<sub>2</sub> produced = 0.4950 g Wt. of H<sub>2</sub>O produced = 0.2025 g Percentage of carbon =  $\frac{12}{44} \times \frac{\text{Wt. of CO}_2}{\text{Wt. of compound}} \times 100$ 

$$=\frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{Wt. of } \text{H}_2\text{O}}{\text{Wt. of compound}} \times 100$$
  
=  $\frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = 9.09$   
8. [2]  
9. [2]  
Theory based  
10. [1]  
Theory based

## EXERCISE # 4

**1.** [1] Lassaigne's test involves the reactions  $\begin{array}{l} \text{Na} + \text{C} + \text{N} \longrightarrow \text{NaCN} \\ \text{Fe}^{2+} + 6\text{CN}^{-} \longrightarrow \left[\text{Fe}(\text{CN})_{6}\right]^{4-} \end{array}$  $\operatorname{Fe}^{3+} + [\operatorname{Fe}(\operatorname{CN})_6]^{4-} \longrightarrow \operatorname{Fe}_4[\operatorname{Fe}(\operatorname{CN})_6]_3$ 2. [3] Amount of H<sup>+</sup> used for the neutralization of NH<sub>3</sub>  $N = 2(0.1 \text{ mol } L^{-1}) (0.1 \text{ L}) - (0.5 \text{ mol } L^{-1})$ (0.02 L) = 0.01 molAmount of N = Amount of  $NH_3$  = Amount of H<sup>+</sup> used = 0.01 molMass of N =  $(0.01 \text{ mol})(14 \text{ g mol}^{-1}) = 0.14 \text{ g}$ Mass per cent of N in the compound =  $\left(\frac{0.14}{0.2g}\right)$ (100) = 46.67%Mass per cent of N in the given compounds are as follows Acetamide (CH<sub>3</sub>CCONH<sub>2</sub>)  $\frac{14}{59} \times 100 = 23.73$ Benzamide (C<sub>6</sub>H<sub>5</sub>CONH<sub>2</sub>) it is less than 23.73 Urea (NH<sub>2</sub>CONH<sub>2</sub>)  $\frac{28}{60} \times 100 = 46.67$ The compound is urea. 3. [4] Volume of 0.1 M HCl taken = 20 mLVolume of 0.1 M NaOH used for neutralisation = 15 mL Volume of 0.1 M HCl unused = 20 - 15 = 5 mL  $\% N = \frac{1.4 \times N \times V(mL)}{W(g)} = 27$ Since n-factor of HCl = 1So, 0.1 M  $\equiv$  0.1 N % N =  $\frac{1.4 \times 0.1 \times 5}{29.5 \times 10^{-3}} = \frac{1.4 \times 1 \times 5}{29.5 \times 10^{-2}} = 23.7$ 4. [1] % of Br =  $\frac{80}{188} \times \frac{\text{Mass of AgBr}}{\text{Mass of organic substance}} \times 100$ 

$$= \frac{80}{188} \times \frac{141}{250} \times 100$$
$$= 24\%$$

5. [1]

Region 1 (Pre-heating zone)

Region 2 (Primary combustion zone, hottest zone)

Region 3 (Internal zone)

Region 4 (Secondary reaction zone)

# 6. [3]

Glycerol with high boiling point (290°C) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points. By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.